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(54) Title: CARBON NANOTUBES AND NESTED FULLERENES SUPPORTING TRANSITION METALS

(57) Abstract

This invention provides a composition, comprising a carbon nanotube and/or a nested fullerene having transition metal particles, clusters, and/or coatings supported thereon; and a method for their preparation; the metal is preferably from the group Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au.

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TITLE

CARBON NANOTUBES AND NESTED FULLERENES SUPPORTING TRANSITION METALS

Field of the Invention

This invention relates to hollow, graphitic tubules of carbon of nanometer dimensions, called nanotubes, and nested fullerenes. Specifically, this invention relates to compositions comprising these nanotubes and nested fullerenes having metals supported thereon, and a method for their preparation.

Background of the Invention

The C_{60} molecule was originally discovered as a peak in the mass spectra of quenched carbon vapor. To explain the stability of this molecule, Kroto et al., "C_{60}: Buckminsterfullerene", *Nature*, 318 (1985) 162-163, first proposed the structure of a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal, commonly encountered as a soccer ball, and dubbed Buckminsterfullerene, or fullerene. Fullerenes may be defined by the following formula: C_n, wherein $n \geq 60$.

Kratschmer et al., "Solid C_{60} a new form of carbon", *Nature*, 347 (1990) 354-358, pioneered the electric arc method for generating fullerenes, which has since become the standard technique.

A simple modification of this technique, increasing the buffer gas, helium, pressure from 100 torr (13,332 Pa) to 500 torr (66,661 Pa), resulted in the formation of carbon nanotubes, as reported by Ajayan et al. in "Large-scale synthesis of carbon nanotubes", *Nature*, 358 (1992) 220-222. The carbon nanotubes consist of nested concentric tubes of carbon where each tube is made up of curved graphite-like sheets of carbon. The tubes are hollow on the inside and the ends of the tube are usually sealed with fullerene-like caps.

The tubes have a high aspect ratio with the diameter being in the range from 2 nanometers to several tens of nanometers and the length being as long as several microns. Also produced are concentric hollow polygons, commonly called nested fullerenes.

As reported by Daniel Ugarte in *Nature*, 359, (1992) 708-709, irradiation with an electron beam can convert nanotubes to concentric hollow spheres.

It has been found possible to open carbon nanotubes with chemical methods as reported by Tsang et al., "Thinning and opening of carbon nanotubes by oxidation using carbon dioxide", *Nature*, 362 (1993) 520-522. Tsang et al. opened the tubes by heating them in carbon dioxide at 850°C. Ajayan et al. opened the tubes by heating the tubes in air above about 700°C, as reported in *Nature*, 362 (1993) 522-525.

Two reports suggest lead and lanthanum carbide can be placed inside carbon nanotubes (Ajayan et al., *Nature* (London), 1993, vol. 361, 333-334; Ruoff et al., Science, 1993, vol. 259, 346-8). During the process of Ajayan et al., lead particles were deposited onto nanotubes following electron beam evaporation of pure lead under vacuum. After annealing in an oven at approximately 400°C, the melting point of lead, the lead particles that had been deposited on closed caps of the tubes appeared to melt and enter the tubes.

An object of the present invention is to provide sealed and unsealed carbon nanotubes and nested fullerenes with supported transition metal particles, clusters of particles, coatings, or a combination thereof attached to the outside surface of the nanotubes and nested fullerenes.

SUMMARY OF THE INVENTION

This invention provides a composition comprising at least one from the group consisting of a carbon nanotube

and a nested fullerene, having at least one transition metal supported thereon, said transition metal being selected from the group consisting of: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt and Au.

This invention also provides a process for the preparation of a composition comprising at least one from the group consisting of a carbon nanotube and a nested fullerene, having at least one transition metal supported thereon, comprising the steps of: reacting at least one of the group consisting of a carbon nanotube and a nested fullerene with at least one metal-complex of the formula L_nM, wherein L = a metal ligand; n is an integer from 1 to 8; and M is a transition metal selected from the group consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt and Au, by slurrying with an inert solvent; isolating the reaction product; and washing the reaction product to remove excess metal complex. In addition the reaction product may be heated under vacuum to a temperature from ambient to about 1000°C, driving off any residual metal-complex from the carbon nanotubes and nested fullerenes with metal particles, clusters, and/or coatings attached thereto.

This invention further provides a composition comprising at least one from the group consisting of a carbon nanotube and a nested fullerene, having at least one transition metal supported thereon, made by a process comprising the steps of: reacting at least one of the group consisting of a carbon nanotube and a nested fullerene with at least one metal-complex of the formula L_nM, wherein L = a metal ligand; n is an integer from 1 to 8; and M is a transition metal selected from the group consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os,

Ir, Pt and Au, by slurrying with an inert solvent; isolating the reaction product; and washing the reaction product to remove excess metal-complex. In addition the reaction product may be heated under vaccuum to a temperature from ambient to about 1000°C.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying photomicrographs, which are incorporated in and constitute a part of the specification, illustrate the presently preferred embodiments of the invention and, together with the general description given above and the detailed description of the preferred embodiments given below, serve to explain the principles of the invention.

FIG. 1A is a photomicrograph of a nanotube with platinum particles, clusters of particles, and a coating supported thereon according to the present invention prior to heat treatment (Example 1).

FIG. 1B is a photomicrograph of nanotubes with platinum particles, clusters of particles, and a coating supported thereon according to the present invention after heat treatment (Example 1).

FIG. 2A is a photomicrograph of a nanotube with palladium particles, clusters, and coating supported thereon according to the present invention prior to heat treatment (Example 2).

FIG. 2B is a photomicrograph of a nanotube with palladium particles, clusters, and coating supported thereon according to the present invention after heat treatment (Example 2).

FIG. 3A is a photomicrograph of a nanotube with nickel particles, clusters and coating supported thereon according to the present invention prior to heat treatment (Example 3).

FIG. 3B is a photomicrograph of a nanotube with nickel particles, clusters and coating supported thereon

according to the present invention after heat treatment (Example 3).

DETAILED DESCRIPTION OF THE INVENTION

This invention provides a composition comprising at least one from the group consisting of a carbon nanotube and a nested fullerene, having at least one transition metal supported thereon, said transition metal being selected from the group consisting of: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt and Au.

For the purpose of the present invention, a carbon nanotube comprises a series of hollow, coaxial tubes, wherein each tube is made up of curved graphite-like sheets of carbon of nanometer dimensions. The nanotubes are hollow on the inside and the ends of the nanotube are usually sealed with fullerene-like caps. The dimensions of the nanotube are about 0.1 to 200 nm in diameter and about 1 to 100 microns in length.

The carbon nanotube of the present invention can be prepared by the procedure of Ajayan et al., in "Large-scale synthesis of carbon nanotubes", *Nature*, 358 (1992) 220-222, incorporated by reference herein.

The composition of the present invention may comprise nanotubes with sealed or unsealed ends. The ends may be unsealed with chemical methods as reported by Tsang et al., "Thinning and opening of carbon nanotubes by oxidation using carbon dioxide", Nature, 362 (1993) 520-522, wherein the tubes were opened by heating them in carbon dioxide at 850°C. Ajayan et al. opened the tubes by heating them in air above about 700°C, as reported in *Nature*, 362 (1993) 522-525.

A nested fullerene of the present invention comprises a series of hollow, concentric spheres or polyhedra of carbon. Nested fullerenes can be prepared

by irradiating a carbon nanotube with an electron beam as reported by Ugarte, *Nature*, 359 (1992) 708-709.

A transition metal is supported by the carbon nanotube and/or nested fullerene of the present invention. For the purpose of the present invention the transition metal is selected from the group consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt and Au. Preferably the transition metal is selected from the group consisting of: Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au; more preferably, Co, Rh, Ir, Ni, Pd and Pt; most preferably, Ni, Pd and Pt. At least one transition metal is supported on the nanotube and/or nested fullerene. As shown in Fig. 1, Fig. 2 and Fig. 3, the transition metal may be in the form of individual metal particles, clusters of metal particles, a coating, or a combination thereof. The particles and clusters range in size from about 0.8 to 20 nm in size, and the coatings are generally less than about 30 Å thick.

Since the chemistry of the outer surface of carbon nanotubes and nested fullerenes is not fully known, for the purpose of the present invention the term "supported" shall mean that the transition metal is attached to the outside surface of the nanotube and/or nested fullerene with the transition metal in the form of particles, clusters of particles, and/or a coating. Since the carbon nanotubes and nested fullerenes have curved carbon surfaces, deposition of metals on these materials results in a unique form of metal on carbon.

This invention also provides a process for the preparation of a composition comprising at least one from the group consisting of a carbon nanotube and a nested fullerene, having at least one transition metal supported thereon, said transition metal from the group

consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt and Au. The process comprises reacting at least one of the group consisting of a carbon nanotube and a nested fullerene (as defined above) with at least one metal-complex of the formula L_nM, wherein L = a metal ligand; n is an integer from 1 to 8; and M is a transition metal selected from the group consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt and Au. Preferably, the transition metal is Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au; more preferably, Co, Rh, Ir, Ni, Pd and Pt; and most preferably, Ni, Pd and Pt. The reaction takes place by slurrying the carbon nanotube and/or nested fullerene with the metal-complex in an inert solvent. Suitable inert solvents are unreactive towards the metal complex. Non-polar hydrocarbons such as alkanes, e.g., hexane, and aromatics, e.g., benzene and toluene, are preferred. Suitable metal ligands are characterized by being labile, that is they are removed upon heating. Examples of organics that are volatile in the temperature range of 25°C to 500°C suitable as a metal ligand are ethylene, ammonia, cyclopentadienyl, cyclooctadiene (C_8H_{16}) and triethylphosphine ($(C_2H_5)_3P$). Cyclooctadiene and triethylphosphine are preferred.

The material is isolated by filtering, centrifuging or decanting and washed with an inert solvent, as described above, to remove excess metal-complex.

Examination by high resolution transmission electron microscopy at this stage in the process shows a material with an amorphous coating of the metal and some remaining ligands. Heating this material in vacuo from ambient to about 1000°C, preferably, about 300°C to 400°C drives off any residual metal-complex ligand, producing the carbon nanotube and/or nested fullerene

with metal particles, clusters of particles and/or coatings attached. The resulting particles and clusters range from about 0.8 to 20 nm in size, and the coatings are generally less than about 30 Å thick.

This invention further provides a composition comprising at least one from the group consisting of a carbon nanotube and a nested fullerene, having at least one transition metal supported thereon, made by a process comprising the steps of: reacting at least one of the group consisting of a carbon nanotube and a nested fullerene with at least one metal-complex of the formula L_nM, wherein L = a metal ligand; n is an integer from 1 to 8; and M is a transition metal selected from the group consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt and Au; preferably, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au; more preferably, Co, Rh, Ir, Ni, Pd and Pt; and most preferably, Ni, Pd and Pt, by slurrying with an inert solvent. Suitable inert solvents are unreactive towards the metal complex. Non-polar hydrocarbons such as alkanes, e.g., hexane, and aromatics, e.g., benzene and toluene, are preferred. After isolating the reaction product by filtering, centrifuging or decanting, the reaction product is washed with an inert solvent, as described above, to remove excess metal-complex. In addition the reaction product may be heated under vaccuum to a temperature from ambient to about 1000°C, preferably about 300°C to 400°C, to form the transition metal supported composition.

General metal on carbon catalysts are used in many industrial applications and activity is found to be extremely structure dependent. Metal supported on various forms of amorphous carbon, which largely contain flat, graphitic sheets of carbon are well known

catalysts. Palladium supported on the surface of carbon particles is particularly useful; for a review, see *Palladium: Recovery, Properties and Uses*, E. M. Wise, Academic Press, New York, 1968. The novel metal and carbon compositions of the present invention in which metal is supported on a curved surface are useful as catalysts in chemical reactions such as hydrogenation of organic substrates, for example, hydrogenation of diphenylacetylene to cis-stilbene and trans-stilbene. Other uses for compositions of the present invention comprise catalyzing reactions, such as dehydrohalogenation, hydrocarbon cracking, and dehydrogenation; fragmentation reactions, such as decarbonylation and decarboxamidation; and isomerization reactions.

The details of the invention at hand can be further understood by reference to the following examples.

EXAMPLE 1

A mixture of carbon nanotubes and nested fullerenes, purchased from Terra Simco Company, Martinsburg, WV, 0.100 g, were placed in a flask with 5-8 ml of hexane. To this was added 0.100 g of $[(C_2H_5)_3P]_4Pt$. This was stirred for 18 hours. The resulting black solid was then isolated by filtration, and washed several times with hexane to remove excess starting material. Examination of a small sample of this material by high resolution transmission electron microscopy revealed the carbon nanotubes are coated with a thin layer of metal-containing amorphous material as shown in Fig. 1A. The solid was dried in vacuo, and then heated to 300°C to 400°C under high vacuum. Examination of the resulting material by high resolution electron microscopy revealed it is made up of carbon nanotubes and nested fullerenes having 10-80 Å platinum clusters attached to the outer surface in some regions,

along with regions coated with a layer or layers of platinum metal as shown in Fig. 1B.

EXAMPLE 2

A mixture of carbon nanotubes and nested fullerenes, purchased from Terra Simco Company, Martinsburg, WV, 0.100 g, were placed in a flask with 5-8 ml of hexane. To this was added 0.100 g of $[(C_2H_5)_3P]_4Pd$. This was stirred for 18 hours. The resulting black solid was then isolated by filtration, and washed several times with hexane to remove excess starting material. Examination of a small sample of this material by high resolution transmission electron microscopy revealed the carbon nanotubes are coated with a thin layer of metal-containing amorphous material. The solid was dried in vacuo, and then heated to 300°C to 400°C under high vacuum. Examination of the resulting material by high resolution electron microscopy revealed it is made up of carbon nanotubes and nested fullerenes having 10-80 Å palladium clusters attached to the outer surface in some regions, along with regions coated with a layer or layers of palladium metal.

EXAMPLE 3

A mixture of carbon nanotubes and nested fullerenes, purchased from Terra Simco Company, Martinsburg, WV, 0.100 g, were placed in a flask with 5-8 ml of hexane. To this was added 0.100 g of $[(C_2H_5)_3P]_4Ni$. This was stirred for 18 hours. The resulting black solid was then isolated by filtration, and washed several times with hexane to remove excess starting material. Examination of a small sample of this material by high resolution transmission electron microscopy revealed the carbon nanotubes are coated with a thin layer of metal-containing amorphous material as shown in Fig. 1A. The solid was dried in vacuo, and

then heated to 300°C to 400°C under high vacuum. Examination of the resulting material by high resolution electron microscopy revealed it is made up of carbon nanotubes having nickel coatings attached to the outer surface in some regions having thicknesses of about 10 to 30 Å.

EXAMPLE 4

A Fisher-Porter bottle was charged with 0.200 g of a mixture of carbon nanotubes and nested fullerenes, purchased commercially from Terra Simco Company, Martinsburg, WV, with palladium supported thereon, heat treated at 400°C in high vacuum, and having approximately 0.5 to 0.8 weight percent palladium, 0.500 g of diphenylacetylene, and 5 mL of toluene. The bottle was attached to a pressure head, and the apparatus was pressurized to 60 psi (4.1×10^5 Pa) of hydrogen gas. The reaction was stirred and heated in an 150°C oil bath for one week. The pressure was released, and the reaction cooled. The toluene solution was filtered from the carbon nanotubes, and was removed in vacuo. Analysis of the product (0.5 g) by ^{1}H NMR revealed a 10% conversion of the diphenyacetylene to cis- and trans-stilbene. The ratio of cis- to trans-stilbene was 80:20. In a control experiment, no hydrogenation was observed in the absence of palladium supported nanotubes, or with carbon nanotubes without supported Pd, under the same conditions.

WHAT IS CLAIMED IS:

1. A composition, comprising: at least one from the group consisting of a carbon nanotube and a nested fullerene, having at least one transition metal supported thereon, said transition metal being selected from the group consisting of: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt and Au.

2. A composition as recited in Claim 1, wherein said transition metal is supported upon said carbon nanotube.

3. A composition as recited in Claim 1, wherein said metal is supported upon said nested fullerene.

4. A composition as recited in Claim 1, wherein said transition metal is selected from the group consisting of: Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au.

5. A composition as recited in Claim 4, wherein said transition metal is selected from the group consisting of: Ni, Pd and Pt.

6. A process for the preparation of a composition comprising at least one from the group consisting of a carbon nanotube and a nested fullerene, having at least one transition metal supported thereon, comprising the steps of:

(a) reacting at least one of the group consisting of a carbon nanotube and a nested fullerene with at least one metal complex of the formula L_nM, wherein L = a metal ligand; n is an integer from 1 to 8; and M is a transition metal selected from the group consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt and Au by slurrying in an inert solvent;

(b) isolating the reaction product; and

(c) washing the reaction product to remove excess metal complex.

7. The process of Claim 6, wherein the complex is $[(C_2H_5)_3P]_4M$ and M is selected from the group consisting of Ni, Pd and Pt.

8. The process of Claim 5, wherein M is selected from the group consisting of Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au.

9. The process of Claim 8, wherein the metal is selected from the group consisting of Ni, Pd and Pt.

10. The process of Claim 6, further comprising the step of:

(a) heating the reaction product under vaccuum to a temperature from ambient to about 1000°C.

11. The process of Claim 10, wherein the temperature is from about 300°C to about 400°C.

12. A composition comprising at least one from the group consisting of a carbon nanotube and a nested fullerene, having at least one transition metal supported thereon, made by a process comprising the steps of:

(a) reacting at least one of the group consisting of a carbon nanotube and a nested fullerene with at least one metal complex of the formula L_nM, wherein L = a metal ligand; n is an integer from 1 to 8; and M is a transition metal selected from the group consisting of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt and Au by slurrying with an inert solvent;

(b) isolating the reaction product; and

(c) washing the reaction product to remove excess metal complex.

13. A composition as recited in Claim 12, wherein the final reaction product is heated under vaccuum to a temperature from ambient to about 1000°C.

14. A composition as recited in Claim 13, wherein the temperature is about 300° to about 400°C.

15. A composition as recited in Claim 12, wherein M is selected from the group consisting of Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au.

16. A composition as recited in Claim 15, wherein M is selected from the group consisting of Ni, Pd and Pt.

17. A composition as recited in Claim 12, wherein the complex is $[(C_2H_5)_3P]_4M$ and M is selected from the group consisting of Ni, Pd and Pt.

FIG. 1A

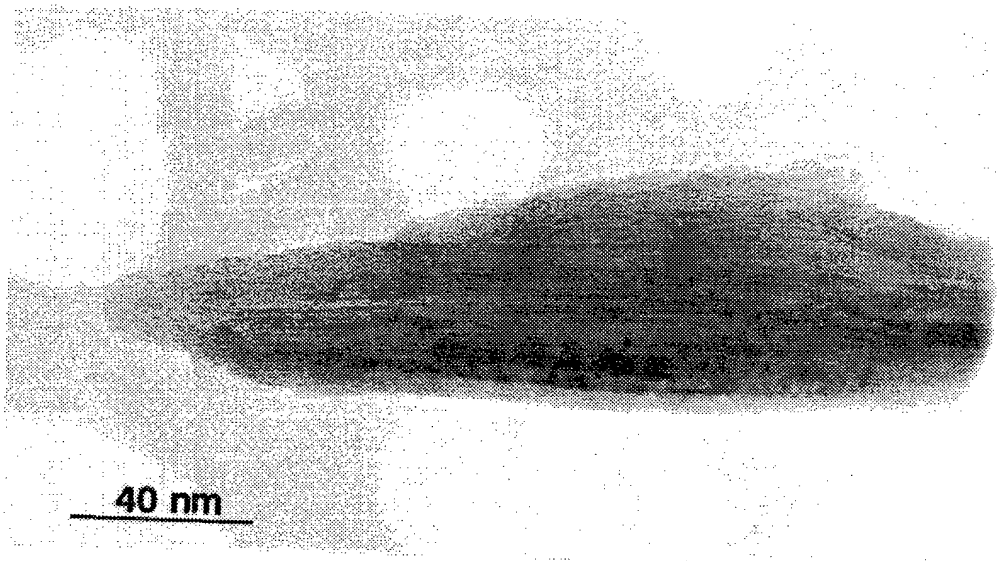


FIG. 1B

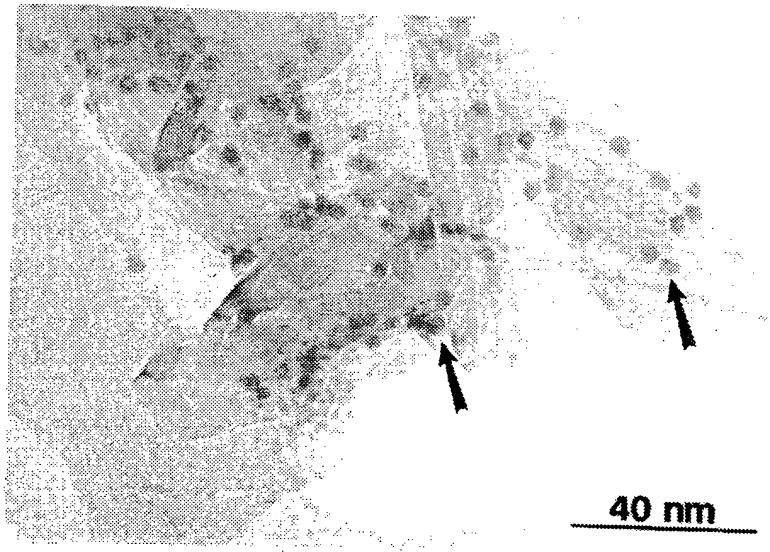


FIG. 2A

FIG. 2B

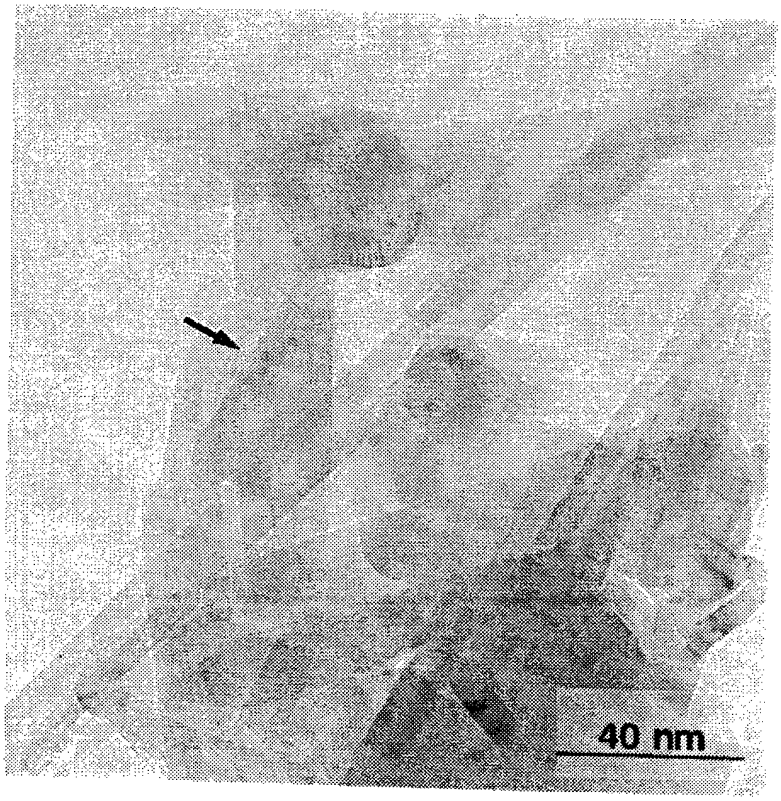
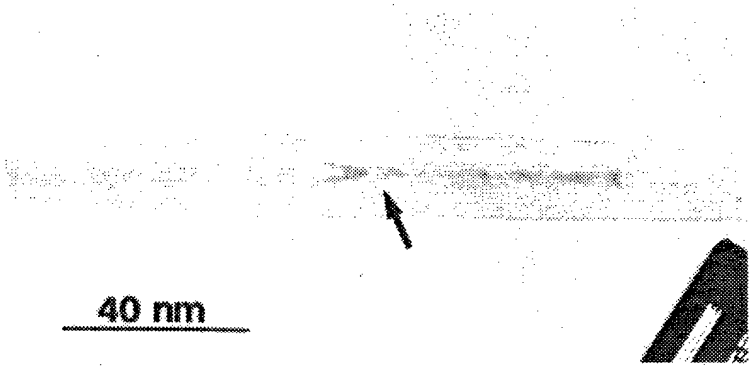


FIG.3A

FIG.3B



INTERNATIONAL SEARCH REPORT

Interna...nal Application No
PCT/US 94/11043

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B31/00 C07F15/04 C07F15/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	NATURE, vol.362, no.6420, 8 April 1993, LONDON GB pages 522 - 525 P. M. AJAYAN ET AL. cited in the application see page 524 : right-hand column : end 1st paragraph ---	1,2,4,5
A	NATURE, vol.361, no.6410, 28 January 1993, LONDON GB pages 333 - 334 P. M. AJAYAN ET AL. cited in the application --- -/--	

[X] Further documents are listed in the continuation of box C.

[ ] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
27 December 1994	10.01.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Brebion, J

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol.116, no.17, 24 August 1994, WASHINGTON, DC US pages 7935 - 7936 J. M. PLANEIX ET AL. see the whole document	1,2,4
A	-----	6,8,10, 12,13,15

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